# TECHNOLOGIC PAPERS

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, Director

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## I. INTRODUCTION

In connection with other investigations on the properties and characteristics of chilled-iron car wheels the question as to the best range of annealing temperatures was raised. Chilled-iron wheels are cast with a chill against the tread and the inside of flange, the remainder being in sand. The composition of the metal is so chosen that under these conditions the tread and inside of the flange will show white iron to a depth of from $\frac{5}{8}$ to $\frac{7}{8}$ inch, the remainder of the wheel becoming graphitized or gray. In order to relieve the stresses set up during cooling under such drastic conditions, the wheels are stripped from the mold while still red hot, piled in a soaking pit, and allowed to cool very slowly from their temperature at stripping.

Obviously the most suitable temperature for this annealing is the highest at which no formation of graphite occurs within the white tread and at which the wheels can be stripped from the molds. Inasmuch as no direct determinations have been made of the temperatures at which the formation of graphite takes place in white iron of compositions used in car wheels upon annealing, it was considered worth while to determine them as a means of establishing the maximum temperatures at which the annealing of the wheels may be carried out. In the course of this work some incidental observations were made which are of interest in connection with the theory of graphitization in white iron.

The literature on the subject of the formation of graphite both during cooling at casting and upon annealing is very extensive and can be best studied by reference to a comprehensive discussion

of the subject by Hatfield.[1]    Perhaps the most important contributions of previous investigation are the following:

1. Whether a given mass of molten iron becomes white, mottled, or gray upon casting depends upon its composition and its rate of cooling through the temperature range of solidification and immediately below.

2. The more rapid the rate of cooling the less is the extent of graphitization.

3. Graphitization increases with increase of carbon or silicon content; it decreases with increasing sulphur content. Manganese plays a double rôle; by combining with the sulphur it first neutralizes the specific effect of the sulphur; an excess of manganese restrains graphitization.

4. Upon annealing irons which have solidified white, the combined carbon decomposes into graphite or temper carbon at temperatures from 700 to 1100° C, depending upon the period of annealing and the composition of the metal. Those elements which promote graphitization upon casting and solidification promote it also during annealing by lowering the temperature range within which decomposition of the cementite is possible.

5. After nuclei of graphite have once formed, further graphitization proceeds more readily and at lower temperatures than in iron of the same composition in which no nuclei are present.

## II. MATERIALS AND ANNEALING

All of the samples used in these experiments were most kindly furnished by the Griffin Wheel Co. through the courtesy of F. K. Vial. Their chemical compositions are given in Table 1.

TABLE 1.—Chemical Compositions of Materials Used

| Heat or series No. | Character | Total carbon | Graphite | Combined carbon | Silicon | Sulphur | Phosphorus | Manganese |
|---|---|---|---|---|---|---|---|---|
| | | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent | Per cent |
| I | White | 3. 67 | 0. 04 | .......... | 0. 57 | 0. 178 | 0. 34 | 0. 53 |
| II | ...do | 3. 68 | . 09 | .......... | . 55 | . 163 | . 33 | . 54 |
| CB | ...do | 3. 78 | . 02 | .......... | . 57 | . 100 | .......... | . 63 |
| CF | ...do | 3. 90 | . 02 | .......... | . 64 | . 204 | .......... | . 63 |
| 5 | Gray | 3. 66 | 2. 80 | 0. 86 | . 63 | . 185 | . 31 | . 58 |

Those samples of the I and the II series were cast in green sand as ¾-inch cubes; those of the CB and CF series were cast in a iron chill mold as cylinders of 1-inch diameter; series "5" was cast

[1] W. H. Hatfield, Cast Iron in the Light of Recent Research, J. B. Lippincott Co.; 1918.

in dry sand as a ¾-inch cube. Series I, II, and 5 were poured from the same heat of metal.

The samples were annealed in an electric furnace of the laboratory type at temperatures and for periods given in Tables 2, 3, and 4. In the earlier part of the work the specimens, being packed in asbestos fiber, were annealed in air. It was found, however, that under these conditions too much decarburization took place at higher temperatures, and the samples were thereafter annealed in a current of dry nitrogen.

In order to keep the temperature constant, as measured by a thermocouple attached to the specimen, during the annealing period, the current for the furnace was in most cases supplied by a generator with a Tirrell regulator giving a constant voltage to within approximately ± 1 per cent. In this manner it was possible to maintain the temperature of the specimen constant during the period of anneal to within approximately ± 5° C. The authors wish to express their appreciation of the aid given by R. W. Woodward in assembling the furnace for annealing and the current-regulating apparatus.

All of the specimens, with the exception of those marked in the table, air-cooled or quenched, were cooled in the furnace to room temperature, a temperature recorder indicating the rate of cooling.

For the three furnaces used these cooling rates are given:

| Furnace | Time required to cool | |
|---|---|---|
| | From 800 to 700° C | From 700 to 300° C |
| | Minutes | Minutes |
| (a)  Platinum wound...................................................... | 19 | 143 |
| (b)  Nichrome............................................................. | 8 | 70 |
| (c)  Nichrome tube........................................................ | 26 | 160 |

The furnace used for each specimen is stated in the tables.

The graphite content of the annealed specimens was determined by a modification of the usual method developed by Dr. E. Schramm, who made many of the analyses reported below. The method consists in dissolving the sample in nitric and hydrofluoric acids and of weighing the insoluble residue after washing. As a check the residue is ignited and weighed again. The total carbon content was determined by combustion and the combined carbon calculated by differences.

The results of all of the determinations are given in Tables 2, 3, and 4. The figures in parentheses represent values obtained on specimens from the same heat, but not on the sample opposite. The results are also summarized in Figs. 1 and 2.

TABLE 2.—Annealing of White Cast Iron, Series I

ANNEALED 6 HOURS IN PLATINUM-WOUND FURNACE; COOLED IN FURNACE

| Specimen | Temperature | Graphite | Combined carbon | Total carbon |
|---|---|---|---|---|
| | ° C | Per cent | Per cent | Per cent |
| Io | As received | 0.05 | (3.61) | (3.64) |
| IC | 700 | .05 | (3.61) | (3.64) |
| ID | 800 | .09 | (3.55) | (3.64) |
| IM | 820 | .12 | (3.52) | (3.64) |
| IN | 840 | .40 | (3.24) | (3.64) |
| IO | 860 | 1.31 | (2.33) | (3.64) |
| IP | 880 | 1.92 | (1.72) | (3.64) |
| IE | 900 | 2.74 | (.90) | (3.64) |
| IS | a 950 | 2.48 | (1.16) | (3.64) |
| IT | 950 | 2.85 | .74 | 3.59 |
| IF | 1000 | 3.25 | .26 | 3.51 |
| IIF | 1000 | 3.27 | .34 | 3.61 |
| IV | b 1000 | 3.44 | .20 | 3.64 |
| IG | 1100 | 2.56 | .70 | 3.26 |
| IU | b 1100 | 3.12 | .52 | 3.64 |

ANNEALED 48 HOURS IN NICHROME FURNACE IN NITROGEN; COOLED IN FURNACE

| Specimen | Temperature | Graphite | Combined carbon | Total carbon |
|---|---|---|---|---|
| IH | 700 | 0.20 | | |
| Ii | 750 | .35 | | |
| IJ | 775 | 1.60 | | |
| IL | 800 | 2.90 | | |
| IQ | 900 | 3.30 | | |
| | 850 | 3.21 | 0.36 | 3.57 |
| IK | c 800 | .74 | | |

a Quenched in water.     b Annealed in nitrogen.     c Annealed 24 hours and cooled in furnace.

TABLE 3.—Annealing of Gray Cast Iron, Series 5

ANNEALED 6 HOURS IN PLATINUM-WOUND FURNACE; COOLED IN FURNACE

| Specimen | Temperature | Graphite | Combined carbon | Total carbon |
|---|---|---|---|---|
| | ° C | Per cent | Per cent | Per cent |
| 5 | As received | 2.80 | 0.86 | 3.66 |
| 5F1 | 600 | 2.87 | (.83) | |
| 5E1 | 700 | 3.08 | (.62) | |
| 5E2 | 700 | 3.02 | .68 | 3.70 |
| 5D1 | 800 | 3.06 | (.64) | |
| 5D2 | 800 | 3.08 | (.62) | |
| 5C1 | 900 | 3.28 | (.42) | |
| 5C2 | 900 | | | |
| 5B | a 1000 | 3.44 | (.26) | |
| 5A | a 1100 | 2.98 | .66 | 3.64 |

a Annealed in nitrogen.

TABLE 4.—Annealing of White Cast Iron; Series CB and CF

ANNEALED 6 HOURS IN NICHROME FURNACE IN NITROGEN; COOLED IN FURNACE

| Specimen | Temperature | Graphite |
|---|---|---|
| | ° C | Per cent |
| CB | As received | 0.02 |
| CB5 | 720 | .02 |
| CB8 | 780 | .04 |
| CB1 | 820 | .83 |
| CB6 | 845 | 2.59 |
| CB11 [a] | 850 | 2.80 |
| CB12 [a] | 870 | 3.38 |
| CB7 | 890 | 3.50 |
| CB13 [a] | 900 | 3.51 |
| CB2 | 920 | 3.45 |
| CB3 | 1020 | 3.42 |
| CB4 | 1120 | 3.25 |
| CF | As received | .02 |
| CF1 | 720 | .03 |
| CF8 | 820 | .13 |
| CF9 | 840 | .94 |
| CF12 [a] | 850 | 2.03 |
| CF6 | 855 | 2.21 |
| CF13 [a] | 870 | 3.33 |
| CF7 | 890 | 3.45 |
| CF14 [a] | 900 | 3.64 |
| CF3 | 920 | 3.48 |
| CF4 | 1020 | 3.72 |
| CF5 | 1120 | 3.47 |

[a] Annealed in nichrome-tube furnace.

## III. DISCUSSION OF RESULTS

It will be observed that for the composition I, the annealing or graphitization range of temperature was much lower for the 48-hour annealing period (700 to 800° C) than for the 6-hour period (800 to 950° C). The range is also narrower. These facts are in accord with experience in the annealing of white iron.

Within the limits of such composition studied the effect of variation of chemical composition upon the graphitization range of temperature was not great. The effect of difference in total carbon content was apparently greater than that of difference in sulphur content. Thus both Series, CB and CF, having higher total carbon content than Series I or II, showed a complete precipitation of temper carbon within a narrower temperature range than did Series I or II, although the temperature of incipient decomposition was very nearly the same in all cases for the 6-hour annealing period. The effect of variation of sulphur content from 0.10 to 0.20 per cent was overshadowed by a variation of total carbon content from 3.60 to 3.90 per cent. It is apparent that the

manganese present in all of the specimens was sufficient to neutralize practically entirely the effect of the sulphur. Microscopic examination of the samples confirmed this view in that a large amount of manganese sulphide was visible. From the standpoint of the commercial annealing of car wheels, the usual variations in chemical composition will not be of any significance. The effect of period of annealing is, however, quite marked, as is seen from consideration of Fig. 1.
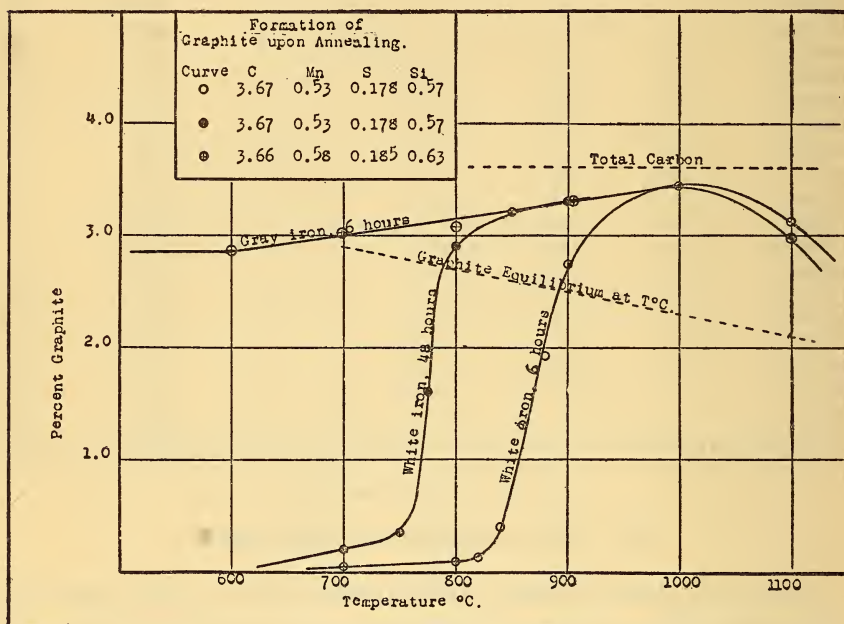


Fig. 1.—*The formation of graphite upon annealing white cast iron. The composition of the iron is given in the upper left corner of the figure*

The maximum allowable temperature for "pitting" wheels is 725° C; above this temperature there is danger of some softening of the tread due to graphitization during annealing.

It is noted also, in entire accord with previous experience, that during a 6-hour anneal the gray-iron Series 5 of the same heat or composition as Series I or II, white, begins to graphitize further at temperatures lower than those at which there is initial graphitization of the white iron.

Attention is invited to the curious fact indicated in the figures, that the specimens annealed at 1100° C and cooled in the furnace showed less graphite, and consequently more combined carbon, than those annealed for the same period at 1000° C and cooled
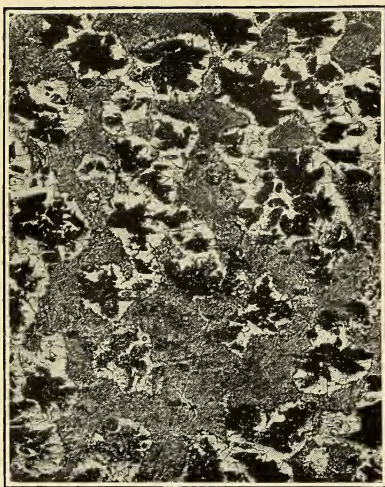
FIG. 3.—*Specimen CB3: annealed six hours at 1,020° C.  ×100*

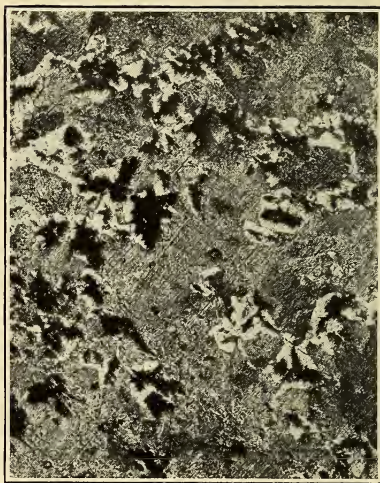FIG. 4.—*Specimen CB4: annealed six hours at 1,120° C.  ×100*
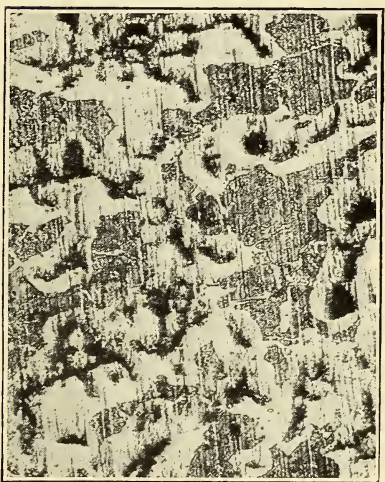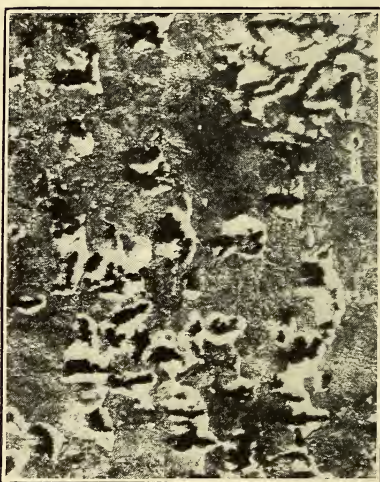
FIG. 5.—*Specimen IF: annealed six hours at 1,000° C.  ×100*

FIG. 6.—*Specimen IU: annealed six hours at 1,100° C.  ×100*

*Microstructure of white cast iron annealed in nitrogen: all specimens etched with 2 per cent nitric acid in alcohol*

at the same rate. This fact was established by several determinations, and is confirmed by microscopic examination of the annealed samples. Figs. 3, 4, 5, and 6 show the microstructure of specimens CB3, CB4, IF, and IU, respectively, after annealing in nitrogen. Specimens CB4 and IU, annealed at 1100°, have more pearlite than specimens CB3 and IF, annealed at 1000° C.
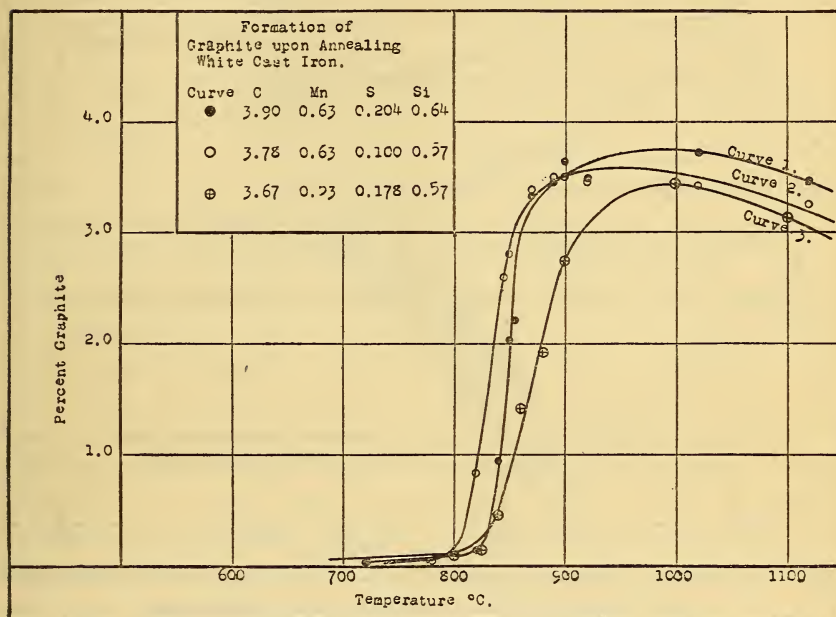


Fig. 2.—*The formation of graphite upon annealing white cast iron. All of the specimens were annealed for 6 hours; their compositions are given on the figure*

In Fig. 7 is reproduced a portion of the equilibrium diagram of the iron-carbon alloys. The line *ES* represents equilibrium between cementite ($Fe_3C$) and solid solution; the line *BJ*, which has never been accurately determined, represents the stable equilibrium between graphite and solid solution.

Upon annealing white iron at increasingly high temperatures, the free cementite is first decomposed into graphite, and the total graphite content is thus increased. At a sufficiently high temperature, about 1000° C, in the instances described above, all of the free cementite has been decomposed, and equilibrium obtains between graphite and solid solution (line *BJ*). Thus, at 1100° there is an amount of carbon in solid solution equal to *C'C*, at 1000°, an amount equal to *F'F*, less than *C'C*. The graphite content of specimens which have attained equilibrium at such

high temperatures, and thereupon been quenched, would be found to correspond to these amounts, as they were in one experiment.

Upon cooling, however, at a more moderate rate, there is sufficient time for crystallization of the graphite upon the nuclei already present, to correspond more closely to equilibrium solu-
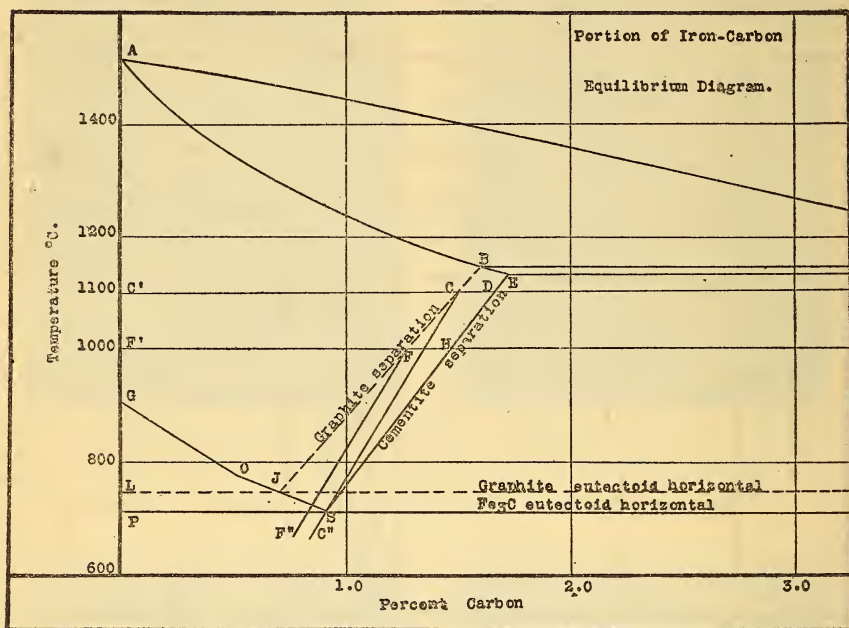


FIG. 7.—*Portion of the iron-carbon equilibrium diagram*

bility. If this precipitation were complete at each moment and equilibrium obtained, the amount of combined carbon in a sample annealed at 1100° and cooled to 1000° would be exactly equal to that in a sample annealed at 1000°; there could be, consequently, no difference in the combined carbon content of the two samples, after cooling at the same rate from this temperature to room temperature.

As a matter of fact, there is a marked difference between the two carbon contents. How is this to be explained?

It is often held that graphitization during cooling from 1100° to 700° C is due to the formation of the temper carbon from cementite, which has previously precipitated along the line *ES*, and that graphite itself can not form directly from the solid solution. Such a theory of the process of the formation of graphite is not capable of explaining the phenomenon described above, since there is no free cementite found after cooling from high temperatures. The

decomposition of the cementite upon its appearance must therefore have proceeded promptly, and the amount of pearlite after complete cooling must have corresponded to the amount present in the pearlite eutectoid.

The graphite must separate directly from the solid solution, but there is apparently a lag in its separation at these rates of cooling. Thus the amount of combined carbon during cooling at any instant must have corresponded to some such values as lie on the line $CC''$ upon cooling from 1000°, and upon the line $FF''$ upon cooling from 1000°. At the temperature of intersection of these lines with the pearlite eutectoid horizontal all of the cementite still remaining in solid solution precipitates as pearlite. The difference in the amount of combined carbon left after cooling from 1100 and from 1000° C is thus explained by the lag in the precipitation of the graphite along its equilibrium curve.

Since the amount of combined carbon finally formed as pearlite in this manner must be greater than the amount of combined carbon at the graphite eutectoid, inasmuch as the lines $FF''$ and $CC''$ lie to the right of line $BJ$ of graphite equilibrium, the results given above would seem to indicate that the graphite eutectoid lies at a smaller value of carbon content than has been previously supposed. At least this is true unless there is either a marked formation of graphite eutectoid at these rates of cooling, or as decomposition of pearlite into graphite, both rather unlikely but not impossible suppositions. The lowest value of combined carbon as pearlite in annealed and slowly cooled specimens found in these experiments was 0.20 per cent; Guertler in his Handbuch der Metallographie gives 0.70 per cent as the most likely amount of carbon in the graphite eutectoid.

The authors have not had an opportunity to continue the study of this phase of the matter, but it would appear that further investigation into the subject of graphitization upon annealing and cooling is needed. An exact determination of the course of the line $BJ$ of graphite equilibrium and of the rate of precipitation of graphite at different temperatures from solid solution would be of much practical value as well as possess scientific interest.

## IV. SUMMARY

1. The annealing or graphitization ranges of temperatures were determined for three different compositions used for car wheels. The temperature of initial precipitation of temper carbon for 6 hours of annealing was not noticeably affected by variation of

sulphur content from 0.10 to 0.20 per cent or by variation of total carbon content from 3.60 to 3.90 per cent, although the effect of greater carbon content is to narrow the temperature range within which graphitization is complete.

2. The temperature of beginning precipitation of temper carbon was about 830° for the 6-hour period of annealing, and about 725° C for the 48-hour period. The maximum allowable temperature, therefore, for the annealing or pitting of car wheels is about 725° C.

3. After complete decomposition of all free cementite by annealing at from 1000 to 1100° C and cooling at equal rates in a laboratory electric furnace less graphite is found in a specimen cooled from a 1100° than in one of the same composition cooled from 1000° C. This indicates that graphite separates directly from solid solution upon cooling, when its nuclei are already present.

4. The fact that only 0.20 per cent of combined carbon was found in some specimens after annealing at high temperatures and cooling slowly in the furnace would indicate either that the graphite eutectoid lies at much lower values of carbon content than has been previously supposed, that there is at those rates of cooling a direct precipitation of graphite eutectoid or that there is a formation of graphite from pearlite at temperatures directly below that of its formation.

WASHINGTON, February 12, 1919.